**13 Titrimetric Methods; Precipitation Titrimetry**

**Titrimetric method**: analytical procedures in which the amount of analyte is determined from the amount of a standard reagent required to react with the analyte completely.

**Three types of quantitative titrimetry**
1. volumetric (the most widely used)
2. gravimetric
3. coulometric

13A Some Terms Used in Volumetric Titrimetry

*Standard solution* (standard titrant)
1. accurate known conc. : 4 significant figures
2. stable
3. stoichiometric reaction : whole-number ratio
4. rapid and quantitatively complete reaction : 99.9 %

*Titration*

*Direct titration*

*Back-titration, residual-titration*: when the rate of reaction between the analyte and reagent is slow or when the reagent lacks stability.

*Equivalence point*, theoretical point: the point in a titration when the amount of added standard reagent exactly equivalent to the amount of analyte.

*End point*: the point in a titration when a physical change occurs that is associated with the condition of chemical equivalence.

*Titration error $E_t$: the difference in volume or mass between the equivalence point and the end point. $(V_{ep} - V_{eq})$*

*Indicator*: large changes in the relative conc. of analyte or titrant occur in the equivalence-point region.
   a. appearance or disappearance of a color.
   b. change in color
   c. appearance or disappearance of turbidity.

Instruments for detect end point: voltmeters, ammeters, ohmmeters, colorimeters, temperature recorders, refractometers.
Fig. 13-1 The titration process

*Primary standards:
1. high purity
2. stability in air
3. absence of hydrate water
4. ready availability at modest cost
5. reasonable solubility in the titration medium
6. reasonably large formula weight

*Secondary standard

13B Standard Solutions

*Standardization, establishing the conc. of standard soln.
1. Direct method: carefully weighed quantity of a primary standard → dissolved → diluted to an exactly known volume.

2. Standardized by titrating

<table>
<thead>
<tr>
<th>Method</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>a.</td>
<td>a weighed quantity of a primary standard</td>
</tr>
<tr>
<td>b.</td>
<td>a weighed quantity of a secondary standard</td>
</tr>
<tr>
<td>c.</td>
<td>a measured volume of another standard soln</td>
</tr>
</tbody>
</table>

*Secondary standard solution |

*Methods for expressing the conc. of standard solutions
a. molarity $C$ : no. of moles/L soln
b. normality $C_N$ : no. of equivalent/L soln.

13C Volumetric calculations

\[
\text{amount } A \text{ (mol)} = \frac{\text{mass } A \text{ (g)}}{\text{molar mass } A \text{ (g/mol)}} = V(L) \times C_A \left(\frac{\text{mol}}{L}\right)
\]

\[
\text{amount } A \text{ (mmol)} = \frac{\text{mass } A \text{ (g)}}{\text{molar mass } A \text{ (g/mmol)}} = V(\text{mL}) \times C_A \left(\frac{\text{mmol}}{\text{mL}}\right)
\]
Ex. 13-1. Describe the preparation of 2.000 L of 0.0500 M AgNO₃ (169.87 g/mol) from the primary standard-grade solid.

- amount AgNO₃ = 0.050 L × 2.000 mol/L = 0.1000 mol
- mass AgNO₃ = 0.1000 mol × 169.87 g/mol = 16.98 g
- dissolving 16.98 g AgNO₃ in water and diluting to 2.000 L.

Ex. 13-2. Describe how 500 mL of standard 0.0100 M Na⁺ solution can be prepared from primary standard Na₂CO₃ (105.99 g/mol).

- amount Na₂CO₃ = 500 mL × 0.0100 mmol/mL × ½ = 2.50 mmol
- mass Na₂CO₃ = 2.50 mmol × 0.10599 g/mmol = 0.265 g
- dissolving 0.265 g Na₂CO₃ in water and diluting to 500 mL.

Ex. 13-3. How would you prepare 50.0-mL portions of SS that are 0.00500 M, 0.00200 M and 0.00100 M in Na⁺ from the soln in Ex. 2?

\[
V_{\text{conc}} \times C_{\text{conc}} = V_{\text{dil}} \times C_{\text{dil}}
\]

\[
V_{\text{conc}} = \frac{V_{\text{dil}} \times C_{\text{dil}}}{C_{\text{conc}}} = \frac{50.0\text{mL} \times 0.00500\text{mmol Na}^+ / \text{mL}}{0.0100\text{mmol Na}^+ / \text{mL}} = 25.0\text{mL}
\]

<table>
<thead>
<tr>
<th>0.00500M</th>
<th>0.00200M</th>
<th>0.00100M</th>
</tr>
</thead>
<tbody>
<tr>
<td>25.0 mL</td>
<td>10.0 mL</td>
<td>5.00 mL</td>
</tr>
</tbody>
</table>

Ex. 13-4. Describe how you would prepare 2.0 L of approximate 0.25 M HClO₄ (100.46 g/mol) from the conc. reagent, which has a specific gravity of 1.67 g/mL and contains 71 % (w/w) HClO₄.

\[ C_{\text{HClO₄}} = 1.67 \text{ (g/mL)} / 0.10046 \text{ (g/mmol)} \times 0.71 = 11.8 \text{ M} \]

no. mmol HClO₄ required = 2000 mL × 0.25 mmol/mL = 500 mmol
vol conc. reagemnt = 500 mmol/11.8 (mmol/mL) = 42.4 conc. reagent
→ diluted about 42 mL of 71 % HClO₄ to 2.0 L.

Ex. 13-5. A 50.00-mL of an HCl solution required 29.71 mL of 0.01963 M Ba(OH)₂ to reach an end point with bromocresol green indicator. Calculate the molarity of the HCl.

\[ \text{Ba(OH)}₂ + 2\text{HCl} \rightarrow \text{BaCl₂} + 2\text{H₂O} \]

1 mmol Ba(OH)₂ reacts with 2 mmol of HCl

- amount Ba(OH)₂ = 29.71 mL × 0.01963 mmol/mL = 0.5832 mmol
- amount HCl = 2 × 0.5832 = 1.1664 mmol

\[
C_{\text{HCl}} = \frac{(29.71 \times 0.01963 \times 2) \text{mmol HCl}}{50.0 \text{ mL soln}} = 0.023328 \text{ M} = 0.0233 \text{ M}
\]
Ex. 13-6. Titration of 0.2121 g pure Na₂C₂O₄ (134.00 g/mol) required 43.31 mL KMnO₄. What is the molarity of the KMnO₄ soln?

\[ 2\text{MnO}_4^- + 5\text{C}_2\text{O}_4^{2-} + 16\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 10\text{CO}_2 + 8\text{H}_2\text{O} \]

stoichiometric ratio = \[\frac{2 \text{ mmol KMnO}_4}{5 \text{ mmol Na}_2\text{C}_2\text{O}_4}\]

amount Na₂C₂O₄ = \[\frac{0.2121 \text{ g}}{0.13400 \text{ g/ mmol}}\]

amount KMnO₄ = \[\frac{0.2121 \text{ mmol} \times \frac{2}{5}}{0.13400 \text{ mmol}}\]

\[C_{\text{KMnO}_4} = \frac{0.2121 \times \frac{2}{5}}{43.31 \text{ mL}} = 0.01462 \text{ M}\]

*Calculation the Quantity of Analyte from Titration Data*

Ex. 13-7. A 0.8040-g sample of an iron ore is dissolved in acid. The iron is then reduced to Fe²⁺ and titrated with 47.22 mL of 0.02242 M KMnO₄ solution. Calculate the results of this analysis in term of (a) % Fe (55.847 g/mol); and (b) % Fe₃O₄ (231.54 g/mol).

\[ \text{MnO}_4^- + 5\text{Fe}^{2+} + 8\text{H}^+ \rightarrow \text{Mn}^{2+} + 5\text{Fe}^{3+} + 4\text{H}_2\text{O} \]

(a). stoichiometric ratio = \[\frac{5 \text{ mmol Fe}^{2+}}{1 \text{ mmol KMnO}_4}\]

amount KMnO₄ = 47.22 mL \times 0.02242 \text{ mol/L} = 1.0587 \text{ mmol}

amount Fe²⁺ = 47.22 mL \times 0.02242 \text{ mol/L} \times 5 = 5.2934 \text{ mmol}

mass Fe²⁺ = 5.2934 \text{ mmol} \times 0.055847 \text{ g/mmol} = 0.2956 \text{ g}

percent Fe²⁺ = \[\frac{(47.22 \times 0.02242 \times 5 \times 0.055847) \text{ g}}{0.8040 \text{ g sample}} \times 100\% = 36.77\%\]

(b). stoichiometric ratio: 5 Fe²⁺ ≡ 1 MnO₄⁻

5 Fe₃O₄ ≡ 15 Fe²⁺ ≡ 3 MnO₄⁻

amount KMnO₄ = 47.22 mL \times 0.02242 \text{ mol/L} = 1.0587 \text{ mmol}

amount Fe₃O₄ = 47.22 mL \times 0.02242 \text{ mol/L} \times 5/3 = 1.76445 \text{ mmol}

mass Fe₃O₄ = 1.76445 \text{ mmol} \times 0.23154 \text{ g/mmol} = 0.4085 \text{ g}

percent Fe₃O₄ = \[\frac{(47.22 \times 0.02242 \times \frac{5}{3}) \times 0.23154 \text{ g}}{0.8040 \text{ g sample}} \times 100\% = 50.81\%\]
Ex. 13-8. A 100.0-mL sample of brackish water was made ammonical, and the sulfide it contained was titrated with 16.47 mL of 0.02310 M AgNO₃. The analytical reaction is \(2\text{Ag}^+ + \text{S}^2- \rightarrow \text{Ag}_2\text{S(s)}\). Calculate \([\text{H}_2\text{S}]\) in the water in ppm.

\[
[H_2S] = \frac{(16.47 \times 0.02310 \times \frac{1}{2}) \times 0.034802g}{100.0\text{ mL} \times 1.000\text{g/mL sample}} \times 10^6 \text{ ppm} = 66.2 \text{ ppm H}_2\text{S}
\]

Ex. 13-9. The phosphorus in a 4.258-g sample of a plant food was converted to \(\text{PO}_4^{3-}\) and precipitated as \(\text{As}_3\text{PO}_4\) through the addition of 50.00 mL of 0.0820 M AgNO₃. The excess AgNO₃ was back-titrated with 4.06 mL of 0.0625 M KSCN. Express the results of the analysis in terms of % \(\text{P}_2\text{O}_5\).

\[
\begin{align*}
\text{P}_2\text{O}_5 + 9\text{H}_2\text{O} & \rightarrow 2\text{PO}_4^{3-} + 6\text{H}_3\text{O}^+ \\
2\text{PO}_4^{3-} + 6\text{Ag}^+_{(excess)} & \rightarrow 2\text{Ag}_3\text{PO}_4(s) \\
\text{Ag}^+ + \text{SCN}^- & \rightarrow \text{AgSCN(s)}
\end{align*}
\]

\[
\%\text{P}_2\text{O}_5 = \frac{(50.00 \times 0.0820 - 4.06 \times 0.0625) \times \frac{1}{6} \times 0.1419\text{g/mmol}}{4.258\text{ g sample}} \times 100\% = 2.14\%
\]

Ex. 13-10. The CO in a 20.3-L sample of gas was converted to \(\text{CO}_2\) by passing the gas over iodine pentoxide heated to 150°C, and \(\text{I}_2\) was distilled and collected to 8.25 mL of 0.01101 M \(\text{Na}_2\text{S}_2\text{O}_3\), then back titration with 2.16 mL of 0.00947 M \(\text{I}_2\) solution. Calculate the mg of CO (28.01 g/mol) per liter of sample.

\[
\begin{align*}
\text{I}_2\text{O}_5(s) + 5\text{CO}(g) & \rightarrow 5\text{CO}_2(g) + \text{I}_2(g) \quad [\text{CO} : \text{I}_2 = 5 : 1] \\
\text{I}_2(aq) + 2\text{S}_2\text{O}_5^{2-}(aq) & \rightarrow 2\text{I}^-(aq) + \text{S}_4\text{O}_6^{2-}(aq) \quad [\text{I}_2 : \text{S}_2\text{O}_5^{2-} = 1 : 2]
\end{align*}
\]

\[
\text{Mass CO} = \frac{(8.25 \times 0.01101 - 2.16 \times 0.00947 \times 2) \times \frac{5}{2} \times 28.01}{20.3\text{ L}} = \frac{0.1248 \text{ mmol} \times 28.01}{20.3} = 3.4956 \times 0.172 \text{ mg/L}
\]

Ex. 11. The organic matter in a 3.776-g sample of a mercuric ointment is decomposed with \(\text{HNO}_3\). After dilution, the \(\text{Hg}^{2+}\) is titrated with 21.30 mL of a 0.1144 M soln of \(\text{NH}_4\text{SCN}\). Calculate the percent \(\text{Hg}\) (200.59 g/mol) in the ointment.

\[
\begin{align*}
\text{Hg}^{2+} + 2\text{SCN}^- & \rightarrow \text{Hg(SCN)}_2(aq) \\
\text{stoichiometric ratio} = 1 \text{ mmol Hg}^{2+}/2 \text{ mmol NH}_4\text{SCN} \\
\text{amount NH}_4\text{SCN} = 21.30 \text{ mL} \times 0.1144 \text{ mmol/mL} = 2.4367 \text{ mmol} \\
\text{amount Hg}^{2+} = 2.4367 \text{ mmol} \times \frac{1}{2} = 1.2184 \text{ mmol} \\
\text{mass Hg}^{2+} = 1.2184 \text{ mmol} \times 0.20059 \text{ g/mmol} = 0.2444 \text{ g}
\end{align*}
\]

\[
\text{percent Hg} = \frac{(21.30 \times 0.1144 \times \frac{1}{2}) \times 0.20059g}{3.776\text{ g sample}} \times 100\% = 6.472\%
\]
Ex. 13-12 A 0.4755-g sample [(NH₄)₂C₂O₄ and inert]/H₂O, added KOH to alkaline [NH₄⁺ → NH₃], distilled into 50.00 mL of 0.05035 M H₂SO₄. Then back titration with 11.13 mL of 0.1214 M NaOH. Calculate (a) the % N (14.007 g/mol) and (b) the % (NH₄)₂C₂O₄ (124.10 g/mol) in the sample.

(a) % N = \( \frac{50.00 \times 0.05035 \times 2 - 11.13 \times 0.1214} {0.4755 \times 1000} \times 100\% \)

= \( \frac{3.6838 \times 14.007} {475.5} \times 100\% = 10.85\% \)

(b) % (NH₄)₂C₂O₄ = \( \frac{3.6838 \times 124.10 / 2} {0.4755 \times 1000} \times 100\% = \frac{228.58} {475.5} \times 100\% \)

= 48.07 %

13D Gravimetric Titrimetry

13 E Titration curves in Titrimetric Methods

(a) Sigmoidal curve
(b) Linear-segment curve

Fig. 13-2
Two types of titration curves.

Table 13-1 Concentration changes during a titration of 50.00 mL of 0.1000M AgNO₃ with 0.1000M KSCN

<table>
<thead>
<tr>
<th>0.1000M KSCN, mL</th>
<th>[Ag⁺] mmol/L</th>
<th>mL of KSCN to cause a tenfold decrease in [Ag⁺]</th>
<th>pAg</th>
<th>pSCN</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>1.000 \times 10⁻¹</td>
<td></td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td>40.91</td>
<td>1.000 \times 10⁻²</td>
<td>40.91</td>
<td>2.00</td>
<td>10.00</td>
</tr>
<tr>
<td>49.01</td>
<td>1.000 \times 10⁻³</td>
<td>8.10</td>
<td>3.00</td>
<td>9.00</td>
</tr>
<tr>
<td>49.90</td>
<td>1.000 \times 10⁻⁴</td>
<td>0.89</td>
<td>4.00</td>
<td>8.00</td>
</tr>
<tr>
<td>49.99</td>
<td>1.000 \times 10⁻⁵</td>
<td>0.09</td>
<td>5.00</td>
<td>7.00</td>
</tr>
<tr>
<td>50.00</td>
<td>1.000 \times 10⁻⁶</td>
<td>0.01</td>
<td>6.00</td>
<td>6.00</td>
</tr>
<tr>
<td>50.01</td>
<td>1.000 \times 10⁻⁷</td>
<td>0.01</td>
<td>7.00</td>
<td>5.00</td>
</tr>
<tr>
<td>50.10</td>
<td>1.000 \times 10⁻⁸</td>
<td>0.09</td>
<td>8.00</td>
<td>4.00</td>
</tr>
<tr>
<td>51.01</td>
<td>1.000 \times 10⁻⁹</td>
<td>0.91</td>
<td>9.00</td>
<td>3.00</td>
</tr>
<tr>
<td>61.11</td>
<td>1.000 \times 10⁻¹⁰</td>
<td>10.10</td>
<td>10.00</td>
<td>2.00</td>
</tr>
</tbody>
</table>
13F Precititation Titrimetry

Silver nitrate titrations: Argentometric methods
for: halides, halide-like anion (SCN⁻, CN⁻, CNO⁻) several divalent anions, mercaptans, fatty acids and several divalent and trivalent inorganic anions.

End point:
1. A change in color due to the reagent, the analyte or an indicator.
2. A change in potential of an electrode that responds to the conc. of one of the reactants.

Titration curves: plots of a conc.-related variable as a function of reagent volume.

13F-1 Precipitation titration curves involving silver ion
♦ preequivalence points
♦ equivalence point
♦ post equivalence points

Ex. 13-13. Perform calculations needed to generate a titration curve for 50.00 mL of 0.0500 M NaCl with 0.1000 M AgNO₃.

Ag⁺(aq) + Cl⁻(aq) ⇌ AgCl(s), \( K_{SP} = [Ag^+][Cl^-] = 1.82 \times 10^{-10} \)

♦ Initial point: 0.000 M in Ag, and pAg is indeterminate.

♦ preequivalence points, At 10.00 mL

\[
[Cl^-] = C_{NaCl} = \frac{\text{original no. mmol Cl}^- \text{ - no. mol AgNO}_3}{\text{total volume of solution}} = \frac{50.00 \times 0.0500 - 10.00 \times 0.100}{50.00 + 10.0} = 0.02500 \text{ M}
\]

\[
[Ag^+] = \frac{K_{SP}}{0.02500} = \frac{1.82 \times 10^{-10}}{0.02500} = 7.28 \times 10^{-9}, \quad pAg = -\log (7.28 \times 10^{-9}) = 8.14
\]
**Equivalence point**

\[
\text{[Ag}^+\text{]} = \sqrt{K_{sp}} = \sqrt{1.82 \times 10^{-10}} = 1.35 \times 10^{-5}, \quad \text{pAg} = -\log (1.35 \times 10^{-5}) = \mathbf{4.87}
\]

**post equivalence point,**

After Addition of 26.0 mL of Reagent

\[
\text{[Ag}^+\text{]} \approx C_{\text{AgNO}_3} = \frac{(26.0 \times 0.1000 - 50.00 \times 0.0500)}{76.00} = 1.316 \times 10^{-3}
\]

\[
\text{pAg} = -\log (1.316 \times 10^{-3}) = \mathbf{2.88}
\]

Tab. 13-2 Changes in pAg in the titration of Cl\(^-\) with AgNO\(_3\).

<table>
<thead>
<tr>
<th>AgNO(_3), mL</th>
<th>50.00 mL of 0.0500 M NaCl with 0.1000M AgNO(_3)</th>
<th>50.00 mL of 0.00500 M NaCl with 0.01000M AgNO(_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.00</td>
<td>8.04</td>
<td>7.14</td>
</tr>
<tr>
<td>20.00</td>
<td>7.59</td>
<td>6.59</td>
</tr>
<tr>
<td>24.00</td>
<td>6.87</td>
<td>5.87</td>
</tr>
<tr>
<td>25.00</td>
<td>4.87</td>
<td>4.87</td>
</tr>
<tr>
<td>26.00</td>
<td>2.88</td>
<td>3.88</td>
</tr>
<tr>
<td>30.00</td>
<td>2.20</td>
<td>3.20</td>
</tr>
<tr>
<td>40.00</td>
<td>1.78</td>
<td>2.78</td>
</tr>
</tbody>
</table>

The shapes of titration curves

Fig. 13-4 Titration curve for A, 50.00 mL of 0.0500 M NaCl with 0.1000 M AgNO\(_3\), and B, 50.00 mL of 0.00500 M NaCl with 0.01000 M AgNO\(_3\).

Fig. 13-5 Effect of reaction completeness on precipitation titration curve, 50.00 mL of a 0.0500 M solution of the anion was titrated with 0.1000 M AgNO\(_3\).

**Factors influencing end-point sharpness**

Satisfactory end points require a change of 2 in p-function within ±0.1 mL of the equivalence point
a. reagent conc. : conc. $\uparrow \rightarrow$ sharpness $\uparrow$

b. reaction completeness : product ppt Ksp $\downarrow \rightarrow$ sharpness $\uparrow$

*Chemical indicators for precipitation titration

$A + R \rightarrow AR(s)$ analyte $A$ with titrant $R$,

$In + R \rightarrow InR$ indicator $In$

For a color change to be seen, $[InR]/[In]$ must change by a factor of 10 to 100.

13F-2 Titration curves for mixtures of anions

Titration of 50.00 mL of a solution ([I$^-$] = 0.0500M and [Cl$^-$]=0.0800 M) with 0.1000 M AgNO$_3$.

$$\frac{[Ag^+][I^-]}{[Ag^+][Cl^-]} = \frac{8.3 \times 10^{-17}}{1.82 \times 10^{-10}} = 4.56 \times 10^{-7} \Rightarrow [I^-] = (4.56 \times 10^{-7})[Cl^-]$$

after added 25.00 mL AgNO$_3$,

$$c_{Cl} = \frac{50.00 \times 0.0800}{50.00 + 25.00} = 0.0533 \text{ M}, \quad [I^-] = 4.56 \times 10^{-7} \times 0.0533 = 2.43 \times 10^{-8} \text{ M}$$

no. mmol $I^-$ = 75.00mL $\times$ (2.43 $\times$ 10$^{-8}$ mmol I$^-$/mL) = 1.82 $\times$ 10$^{-6}$

$I^-$ unprecipitated $= \frac{1.82 \times 10^{-6}}{50.00 \times 0.0500} \times 100\% = 7.3 \times 10^{-5} \%$

$$[Ag^+] = \frac{1.82 \times 10^{-10}}{0.0533} = 3.41 \times 10^{-9} \Rightarrow pAg = -\log(3.41 \times 10^{-9}) = 8.47$$

after added 30.00 mL AgNO$_3$,

$$c_{Cl} = [Cl^-] = \frac{50.00 \times 0.0800 + 50.00 \times 0.0500 - 30.00 \times 0.100}{50.00 + 30.00} = 0.0438 \text{ M}$$

$$[Ag^+] = \frac{1.82 \times 10^{-10}}{0.0438} = 4.16 \times 10^{-9}, \quad pAg = 8.38$$

Fig. 13-6 Titration curves for 50.00 mL of a solution 0.0800 M in Cl$^-$ and 0.0500 M in I$^-$ or Br$^-$.  
AgI: $K_{sp} = 8.3 \times 10^{-17}$

AgBr: $K_{sp} = 5.2 \times 10^{-13}$

AgCl: $K_{sp} = 1.8 \times 10^{-10}$
13F-3 Indicators for Argentometric Titrations

*AgNO₃ titrations

<table>
<thead>
<tr>
<th>Method</th>
<th>Mohr (Direct)</th>
<th>Fajans (Direct)</th>
<th>Volhard (Residual)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titrant</td>
<td>AgNO₃</td>
<td>AgNO₃</td>
<td>AgNO₃-KSCN</td>
</tr>
<tr>
<td>Indicator</td>
<td>Na₂CrO₄</td>
<td>Fluorescein</td>
<td>Fe³⁺ (red ppt)</td>
</tr>
<tr>
<td>End point</td>
<td>Ag₂CrO₄(s) red</td>
<td>AgX:Ag⁺ · · Fl⁺(s) red</td>
<td>Fe(SCN)²⁺ red solution</td>
</tr>
<tr>
<td>Titration pH</td>
<td>6.5 ~ 10.3</td>
<td>≥7</td>
<td>Acidic</td>
</tr>
</tbody>
</table>

1. Chromate Ion; The Mohr method

1865 K. F. Mohr, a German pharmaceutical chemist

Sample: Cl⁻, Br⁻, CN⁻

\[
\text{AgNO}_3 + X^- \rightleftharpoons \text{AgX(s) + NO}_3^- \\
\text{AgNO}_3 + \text{CN}^- \rightleftharpoons \text{Ag(CN)}_2^-(aq) + \text{NO}_3^-
\]

End point: \(2\text{AgNO}_3 + \text{CrO}_4^{2-} \rightleftharpoons \text{Ag}_2\text{CrO}_4(s) + 2 \text{NO}_3^- \)

Yellow \(\rightleftharpoons\) red (\(K_{sp} = 1.1 \times 10^{-12} \text{ M}^3\))

Not for arsenate, I⁻, SCN⁻

Solubility: \(\text{Ag}_2\text{CrO}_4 > \text{AgX}\)

*Choice of indicator:

If indicator- I⁻ anion (AgI \(K_{sp} = 8.3 \times 10^{-17} \text{ M}^2\))

\[
\text{AgCl} \ K_{sp} = 1.82 \times 10^{-10} \text{ M}^2 \\
[\text{Ag}^+]_{ep} = (K_{sp})^{1/2} = (1.82 \times 10^{-10} \text{ M}^2)^{1/2} = 1.35 \times 10^{-5} \text{ M}
\]

If indicator- I⁻ anion conc. = 0.0025 M

AgI ppt formation

\[
[\text{Ag}^+]_{min} = 8.3 \times 10^{-17} \text{ M}^2/0.0025 \text{ M} = 3.3 \times 10^{-14} \text{ M}
\]

Pre-equivalence point: \(\text{Ag}^+ \rightarrow \text{AgI(s)}\)

*Concentration of indicator \([\text{CrO}_4^{2-}]\)

Equivalence point: \( [\text{Ag}^+] = [\text{Cl}^-] = 1.35 \times 10^{-5} \text{ M} \)

\( [\text{CrO}_4^{2-}] = K_{sp}/[\text{Ag}^+]^2 = 1.2 \times 10^{-12}/(1.35 \times 10^{-5})^2 = 6.6 \times 10^{-3} \text{ M} \)

*pH : 6.5 ~ 10.3 (7~10)

\(\text{pH} < 6.5 \quad \text{Ag}_2\text{CrO}_4(s) \rightleftharpoons 2\text{Ag}^+ + \text{CrO}_4^{2-} \)

\( \text{CrO}_4^{2-} + \text{H}^+ \rightleftharpoons \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O} \)

\(\text{pH} > 10.3 \quad \text{Ag}^+ + \text{OH}^- \rightleftharpoons \text{AgOH(s)}\)
2. Adsorption indicators: The Fajans method

1926, Polish chemist, K. Fajans
Advantages: rapid, accurate and reliable

\[
\text{AgNO}_3 + \text{X}^- \rightleftharpoons \text{AgX(s) + NO}_3^- \\
\]
End point:

\[
\text{Ag}^+ + \text{AgX(s) + Fl}^- \rightleftharpoons \text{AgX:Ag}^+ \cdot \cdot \text{ Fl}(s) \\
\]

Yellow-green    red

Indicator: Fluorescein anion

* avoid ppt coagulation → ppt surface ↑
  a. adding dextrin or polyethylene glycol
  b. quick titration and avoid excessive stirring
  c. halide ion conc. : 0.005 ~ 0.025 M

*Fluorescein dyes: weak ionized acids
  \[\text{pH} \downarrow \rightarrow [\text{Fl}^-] \downarrow \rightarrow \text{weak end point}\]
  \[\text{pH} \geq 7, \text{ (dichlorofluorescein: pH} \geq 4)\]

*Photochemical decomposition : ppt → black

<table>
<thead>
<tr>
<th>Indicator</th>
<th>pH</th>
<th>Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorescein</td>
<td>≥7</td>
<td>Cl⁻, Br⁻, I⁻, SCN⁻</td>
</tr>
<tr>
<td>Dichlorofluorescein</td>
<td>≥4</td>
<td>Cl⁻, Br⁻, I⁻, SCN⁻</td>
</tr>
<tr>
<td>Eosin</td>
<td>≥2</td>
<td>Br⁻, I⁻, SCN⁻</td>
</tr>
</tbody>
</table>

3. Iron(III) Ion; The Volhard method

1874 Jacob Volhard, a German chemist, (back titration): Iron(III) ion as indicator

sample: halide ion, C₂O₄²⁻, AsO₄³⁻, SCN⁻

\[\text{nAgNO}_3 \text{ (excess) + B}^n- \rightleftharpoons \text{Ag}_n\text{B(s) + nNO}_3^- \]

\[\text{KSCN + unreacted AgNO}_3 \rightleftharpoons \text{AgSCN(s) + K}^+ + \text{NO}_3^- \]

End point:

\[\text{Fe}^{3+} + \text{SCN}^- \rightleftharpoons \text{Fe(SCN)}^{2+} \text{ red} \]

\[K_r = \frac{[\text{Fe(SCN)}^{2+}]}{[\text{Fe}^{3+}][\text{SCN}^-]} = 1050 \]

*pH : in acidic soln to prevent Fe(III) → Fe(OH)₃(s)
  *advantage: carbonate, oxalate & arsenate do not interfere.
  *For Cl⁻ ion in blood serum, urine. (sample: HNO₃ digestion)

*Quantitativeness of the back titration

\[\text{n SCN}^- + \text{Ag}_n\text{B(s)} \rightleftharpoons \text{n AgSCN(s) + B}^n- \]

a. compare AgSCN and AgₙB : molar solubility \[\text{AgSCN: } 1.0 \times 10^{-6} \text{ M} \]
b. Calculate $K_{rxn}$

$$K_{rxn} = \frac{[B^{n-}]}{[SCN^{-}]^n} = \frac{K_{sp \ of \ Ag_nB}}{(K_{sp \ of \ AgSCN})^n}$$

if $AgSCN$ solubility $< Ag_nB$ or $K_{rxn} > 1$

→ filter $Ag_nB$ ppt or adding liquid nitrobenzene

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<tr>
<th>Analyte</th>
<th>End point</th>
<th>Remarks</th>
</tr>
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<td>$AsO_4^{3-}$, $Br^-$, $I^-$, $CNO^-$, $SCN^-$</td>
<td>Volhard</td>
<td>Removal of Ag salt not required</td>
</tr>
<tr>
<td>$CO_3^{2-}$, $CrO_4^{2-}$, $CN^-$, Volhard</td>
<td>Removal of Ag salt required before back-titration of excess Ag$^+$</td>
<td></td>
</tr>
<tr>
<td>$Cl^-$, $C_2O_4^{2-}$, $PO_4^{3-}$, $S^2$-, $NCN^2$-</td>
<td>Volhard</td>
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</tr>
<tr>
<td>$BH_4^-$</td>
<td>Modified Volhard</td>
<td>Titration of excess Ag$^+$ following $BH_4^- + 8Ag^+ + 8OH^- \rightarrow 8Ag(s) + H_2BO_3^- + 5H_2O$</td>
</tr>
<tr>
<td>Epoxide</td>
<td>Volhard</td>
<td>Titration of excess Cl$^-$ following hydrohalogenation</td>
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<td>$K^+$</td>
<td>Modified Volhard</td>
<td>Precipitation of K$^+$ with known excess of $B(C_6H_5)_4^-$, addition of excess Ag$^+$ giving $AgB(C_6H_5)_4(s)$, and back-titration of the excess</td>
</tr>
<tr>
<td>$Br^-$, $Cl^-$</td>
<td>Mohr method</td>
<td>In neutral solution</td>
</tr>
<tr>
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<tr>
<td>$V(OH)_4^+$, fatty acids, mercaptans</td>
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<tr>
<td>$Zn^{2+}$</td>
<td>Modified Volhard</td>
<td>Precipitation as ZnHg(SCN)$_4$, filtration, dissolution in acid, addition of excess Ag$^+$, back-titration of excess Ag$^+$</td>
</tr>
<tr>
<td>$F^-$</td>
<td>Modified Volhard</td>
<td>Precipitation as PbCIF, filtration, dissolution in acid, addition of excess Ag$^+$, back-titration of excess Ag$^+$</td>
</tr>
</tbody>
</table>

Ex. The As in a 9.13-g sample of pesticide was converted to $AsO_4^{3-}$ and precipitated as $Ag_3AsO_4$ with 50.00 mL of 0.02015 M $AgNO_3$. The excess $Ag^+$ was then titrated with 4.75 mL of 0.04321 M $KSCN$. Calculate the % of $As_2O_3$ in the sample.

no. mmol $AgNO_3 = 50.00 \ mL \times 0.02015 \ mmol = 1.0075$

no. mmol $KSCN = 4.75 \ mL \times 0.04321 \ mmol = 0.2052$

no. mmol $AgNO_3$ consumed by $AsO_4^{3-} = 0.8023$

$As_2O_3 \equiv 2 \ AsO_4^{3-} \equiv 6 \ AgNO_3$

$% As_2O_3 = 0.8023 \times (1/6) \times 0.1978/9.13 \times 100\% = 0.2987\%$
*Quantitiveness of AgNO₃ titration*

\[ \text{Ag}^+ + \text{X}^- \Leftrightarrow \text{AgX(s)} \quad \text{Krxn} = \frac{1}{K_{sp}} = \frac{1}{[\text{Ag}^+][\text{X}^-]} \]

a. **99.9 % reaction**: at equivalence point, max % Cl⁻ : 0.1 %

ex: AgCl, Ksp = 1.8 × 10⁻¹⁰;  \[ [\text{Cl}^-] = \sqrt{K_{sp}} = 1.34 \times 10^{-5} \text{ M} \]

\[
\%\text{dissolved} = \frac{\sqrt{K_{sp} \text{ of AgCl}} \times 100}{\text{M of initial Cl}^-} = \frac{1.34 \times 10^{-5} \times 100}{0.010 \text{ M}} = 0.13\%
\]

b. min. theo. Krxn ↔ Krxn

Krxn = 1/Ksp

0.10 M sample [X⁻] → 0.1 %

upper limit of [X⁻] = (0.10 M)(0.1 %) = 10⁻⁴ M

equivalence point : [Ag⁺] = [X⁻]

\[
\text{min theo. } K_{rxn} = \frac{1}{(10^{-4} \text{ M Ag}^+)(10^{-4} \text{ M X}^-)} = 10^8
\]

for 0.1 M X⁻, actual Krxn ≥ 10⁸

for 0.01 M X⁻, actual Krxn ≥ 10¹⁰